

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 December 2000 (07.12.2000)

PCT

(10) International Publication Number
WO 00/73202 A1

(51) International Patent Classification⁷: C01B 21/22

(21) International Application Number: PCT/US99/25597

(22) International Filing Date:
1 November 1999 (01.11.1999)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/320,077 26 May 1999 (26.05.1999) US

(71) Applicant: SOLUTIA INC. [US/US]; 575 Maryville Center Drive, St. Louis, MO 63141 (US).

(72) Inventors: NOTTE, Patrick; 412 Kilkenny Way, Cantonment, FL 32533 (US). BOWMAN, Barry, L.; 6059 Forest Green Road, Pensacola, FL 32505 (US). OPPENHEIM, Judith, P.; 13 Port Royal Way, Pensacola, FL 32501 (US). NOSKOV, Alexandr, Stepanovich; pr. Tsetnoi 9-14, Novosibirsk, 630090 (RU). CHANDRASEKHAR, Ramoorthy; 100 Birchleaf Lane, Greer, SC 29650 (US). CROCE, Greg; 4490 Deerberry Ct., Concord, CA 94521 (US).

(74) Agent: LUNDELL, Craig, M.; Arnold White & Durkee, 750 Bering Drive, Houston, TX 77057-2198 (US).

(81) Designated States (*national*): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR NITROUS OXIDE PURIFICATION

(57) Abstract: A method for purification of a nitrous oxide gas by feeding the nitrous oxide gas and a reducing agent into a de-oxidation reactor, performing de-oxidation by reacting the reducing agent with oxygen using a catalyst in order to deplete the oxygen in the nitrous oxide gas, while limiting the amount of nitrous oxide removed from the nitrous oxide gas.

WO 00/73202 A1



- 1 -

PROCESS FOR NITROUS OXIDE PURIFICATION

FIELD OF THE INVENTION

The present invention relates to a process for purifying a nitrous oxide gas by removal of various impurities.

BACKGROUND OF THE INVENTION

5 A number of processes for purification of off-gases and exhaust gases produced from various thermal power plants are known in the art. Such gases contain undesirable components, such as NO_x (nitrogen oxides including NO, N₂O₃, NO₂, N₂O₄, N₂O₅, etc.), sulfur oxides, and the like. These processes are based either on absorption of such impurities by liquid absorbents, 10 or on their conversion (reduction) into harmless compounds (e.g., water vapor and nitrogen in the case of NO_x reduction). The most widely employed processes for reduction of NO_x use ammonia and selective catalytic reduction (SCR). The SCR processes make it possible to carry out the reduction of NO_x to elemental nitrogen and water vapor in the presence of oxygen contained in the off-gases. See U. S. Patents Nos. 5,401,479; 4,859,439; 4,855,115; 4,789,533; 15 4,438,082; 4,720,476; 4,695,438; 4,732,743; 4,975,256; 4,521,388; 5,401,478; and 5,753,582, the entire subject matter of which is incorporated herein by reference. After off-gases are cleaned of minor impurities by conventional processes/equipment, they are vented to the atmosphere.

Moreover, there are also known processes for purifying various commercial grade gases, 20 such as inert gases. For example, U. S. Patent No. 4,579,723, the entire subject matter of which is incorporated by reference, utilizes a multi-step catalytic process to remove CO, CO₂, H₂, H₂O, and O₂ from an argon gas.

Various processes have been utilized for removing O₂ from very pure nitrous oxide gas produced from stand alone commercial processes for subsequent use in semiconductor 25 manufacturing. In Japanese Kokai No. 06016402, oxygen is removed from commercially produced nitrous oxide using a manganese oxide catalyst. However, oxygen is removed by using oxygen present in the gas to oxidize the catalyst from a lower to a higher manganese oxide, which does not involve catalysis of reactions involving oxygen containing gases to form easily removed products.

30 Heretofore, removal of impurities from nitrous oxide off-gases has not been contemplated. Releasing nitrous oxide off-gases into the environment is a source of pollution and a waste of nitrous oxide that, if economically and feasibly separated from such off-gases to

- 2 -

provide a commercial grade nitrous oxide source, could lead to its use in various processes, such as for use in conversion of benzene to phenol by hydroxylation. See U. S. Patents Nos. 4,982,013; 5,001,280; 5,055,623; 5,110,995; 5,672,777; 5,756,861 and 5,808,167, the entire subject matter of which is incorporated herein by reference. Accordingly, there is a need in the chemical industry for a process that purifies nitrous oxide off-gases and at the same time commercially and economically produces nitrous oxide suitable for various commercial applications.

SUMMARY OF THE INVENTION

The present invention relates to a method for purification of a nitrous oxide gas by feeding the nitrous oxide gas and reducing agent or precursor thereof into a de-oxidation reactor, and performing de-oxidation by reacting the reducing agent or precursor thereof with oxygen using a catalyst to form an inert, in order to deplete the oxygen in the nitrous oxide gas, while limiting the amount of nitrous oxide removed from the nitrous oxide gas.

Additionally, the present invention concerns a method for purification of a nitrous oxide gas by feeding the nitrous oxide gas and ammonia or a precursor thereof into a reactor system, performing selective catalytic reduction by reacting the ammonia or precursor thereof with NOx in the nitrous oxide gas using a selective catalytic reduction catalyst, feeding hydrogen or a precursor thereof into the reactor system and performing de-oxidation by reacting the hydrogen or a precursor thereof with oxygen in the nitrous oxide gas using a de-oxidation catalyst.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be more clearly understood by reference to the following description of exemplary embodiments thereof in conjunction with the attached drawings, which represent data obtained as a result of an embodiment of a process according to the invention as set forth in EXAMPLES I and II.

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

In accordance with the present invention, a nitrous oxide off-gas is purified utilizing catalytic processes to provide an economical source of nitrous oxide suitable for various commercial applications. Moreover, the process of the present invention selectively purifies nitrous oxide off-gas while maintaining the amount of nitrous oxide in the off-gas by selectively reacting out selected impurities in the off-gas. Such a purified nitrous oxide off-gas may be utilized in one-step hydroxylation of benzene to phenol, as set forth in U. S. Patents Nos.

- 3 -

4,982,013; 5,001,280; 5,055,623; 5,110,995; 5,672,777; 5,756,861 and 5,808,167, the entire subject matter of which is incorporated herein by reference.

In one embodiment of the present invention, nitrous oxide off-gas is passed through an SCR reactor in the presence of ammonia or a precursor thereof to remove (e.g., by reacting) NO_x while at the same time not reducing the amount of nitrous oxide in the off-gas. The reactor comprises at least one catalyst bed and may be of any suitable configuration such as fixed bed reactor, (e.g., metal, parallel plate, ceramic honeycomb, tubular, or a lateral flow reactor). Preferably, the reactor is a lateral flow reactor. A lateral flow reactor allows a pellet type of catalyst to be employed in a fixed bed providing a higher contact efficiency at a lower pressure drop than a honeycomb catalyst in the same service. Intimate mixing between the ammonia vapor and process gas is accomplished with the use of perforated plates.

The catalyst may comprise any known NO_x abatement SCR catalyst, such as those based on transition metals, e.g., Ti, V, W, Mo, Mn, Cu, Fe, Cr, Co, Ni, Zn, Sn, etc. The metal may be in the form of an oxide and may be integrated with or placed on a conventional carrier, such as silica and/or alumina. Preferably, an oxide of Ti-V catalyst is used.

The catalyst pellets may be formed into any shape, such as cylinders, spheres, discs, rings, etc., or in the form of a honeycomb block and utilized under conventional SCR conditions. These conditions are dictated by the space velocity of the catalyst, its operating temperature, and the NO_x loading.

For example, ammonia or a precursor thereof is mixed with the nitrous oxide off-gas containing NO_x at a molar ratio with respect to the NO_x from 0.1 to 2.0, preferably 0.5 to 1.5, and more preferably from 0.8 to 1.2. The mixture may be at a temperature from 100°C to 600°C, preferably from 120°C to 400°C, and more preferably from 150°C to 300°C. For adipic acid off-gas service where nitrous oxide is to be preserved, a low temperature range between 150 to 350°C is preferable. Space velocities (amount of gas in cubic meters that passes in one hour through one cubic meter of the catalyst (apparent volume of the catalyst bed) stated with the dimension reciprocal hour) in the range from 300 to 100,000 h⁻¹ may be utilized. The process may be conducted under any pressure. However suitable pressures range from about 1 to about 10 atmospheres.

- 4 -

The ammonia or precursor thereof reacts with the NO_x to form N₂ and H₂O. The nitrous oxide exiting the reactor comprises less than 200 ppm of NO_x, preferably less than 40 ppm, and more preferably less than 10 ppm.

Prior to entering the reactor, ammonia and a carrier gas are mixed together. The carrier
5 gas may contain any inert gas that does not significantly deactivate the catalyst. For example, the carrier gas may contain steam, hydrogen, argon, etc., or mixtures thereof. Preferably the carrier gas contains steam.

In another embodiment of the present invention, nitrous oxide off-gas is passed through
10 at least one reactor in the presence of a reducing agent or precursor thereof and a catalyst to remove oxygen and other impurities, such as organics (e.g., CO, etc.) without reducing the amount of nitrous oxide present in the off-gas. The reactor comprises at least one catalyst bed and may be of any suitable configuration such as a fixed bed, a tubular reactor, or a lateral flow reactor. Preferably, the reactor is a fixed bed reactor.

The catalyst may comprise any known oxidation catalyst, such as those based on a noble
15 metal or combination of noble metals (e.g., platinum or palladium, etc.). The catalyst may be integrated with or placed on a conventional carrier, such as silica and/or alumina. Preferably, the catalyst is a palladium metal with an alumina support.

The catalyst may be formed into any shape, such as cylinders, spheres, discs, rings, etc.,
or in the form of a honeycomb block. Preferably, the catalyst is in the form of a honeycomb
20 block.

In this embodiment of the present invention, stoichiometric amounts of a reducing agent
or precursor thereof is mixed with the nitrous oxide off-gas containing oxygen. The mixture may be at a temperature from 0°C to 600°C, preferably from 5°C to 300°C, and more preferably from 10°C to 200°C. Space velocities (amount of gas in cubic meters that passes in one hour
25 through one cubic meter of the catalyst (apparent volume of the catalyst bed) stated with the dimension reciprocal hour) in the range from 300 to 100,000 h⁻¹ may be utilized. The process may be conducted under any pressure. However suitable pressures range from about 1 to about 10 atmospheres.

The reducing agent or precursor thereof may be mixed with the nitrous oxide off-gas
30 prior to entering the reactor, or in the reactor itself. This may be accomplished using conventional means, such as an inline mixer. Suitable reducing agents include agents that

- 5 -

selectively react with oxygen in the nitrous oxide off-gas without depleting the nitrous oxide in the off-gas. For example, the reducing agent may be hydrogen, which selectively reacts (using an appropriate catalyst as described herein) with oxygen present in the off-gas to produce water. In an embodiment of the present invention, it has been discovered that the hydrogen
5 unexpectedly does not deplete the nitrous oxide in the off-gas (hydrogen would have been expected to also react with nitrous oxide to form nitrogen and water. Another suitable reducing agent is, for example, carbon monoxide, which selectively reacts with oxygen to form carbon dioxide without depleting the nitrous oxide present in the off-gas. The reducing gas may contain a mixture of gases, such as hydrogen and carbon monoxide. Preferably, the reducing gas is a
10 hydrogen containing gas. The hydrogen may be provided in any form, including any hydrogen containing gas such as hydrogen plant offgas, offgas from a dehydrogenation process (e.g. ethylbenzene to styrene), etc. Preferably, the hydrogen is provided in the form of pure hydrogen.

In another embodiment of the present invention, the nitrous oxide off-gas is passed
15 through an SCR reactor to remove NOx utilizing the NOx abatement process of the present invention and subsequently the nitrous oxide off-gas is passed through a de-oxidation reactor to remove oxygen and other impurities using the de-oxidation process of the present invention. Alternatively, the de-oxidation process may precede the NOx abatement process. Moreover, such processes may be conducted multiple times and in any order. The NOx abatement and de-
20 oxidation processes may be conducted in a single reactor having multiple catalyst beds or in a single reactor having multiple chambers. Additionally, each of the NOx abatement and de-oxidation processes may be conducted utilizing multiple reactors. Preferably, NOx abatement precedes de-oxidation.

The recovery of nitrous oxide from the nitrous oxide off-gas utilizing the present
25 purification system comprises greater than 50%, preferably greater than 70%, and more preferably greater than 95%.

EXAMPLES

Processes of the present invention are further defined by reference to the following illustrative examples.

- 6 -

EXAMPLE I

A process for purification of a nitrous oxide gas of the present invention is performed as follows:

5 A 0.2% w/w Pd on alumina catalyst in the form of beads from Johnson-Matthey is exposed to a gas stream of 60 cc/min composed of 2.4 cc/min of oxygen, 36 cc/min of nitrous oxide, and 6 cc/min of helium at 150°C in a quartz reactor. Contact time is 4.6 seconds. Part of the helium gas is gradually replaced by pure hydrogen. Reaction is followed up by analysis of the reactor effluent by mass spectrometry (amu 32 for oxygen, amu 28, 30 and 44 for nitrous oxide, amu 2 for hydrogen, amu 18 for water). Complete reaction of hydrogen is observed in all
10 the tested cases. Figures 1 and 2 illustrate the selective reaction of oxygen with hydrogen, and not with nitrous oxide, respectively. Figure 1 shows the oxygen destruction as a function of the hydrogen flow. Figure 2 demonstrates the percent nitrous oxide destruction as a function of the hydrogen flow. Figure 3 represents the oxygen destruction selectivity as a function of the hydrogen flow.

EXAMPLE II

15 The same experiment is conducted at 25°C with a contact time of 0.7 sec with the same gas stream composition and velocities. Figures 4 and 5 demonstrate the performance achieved in this set of conditions. Figure 4 shows the oxygen destruction as a function of the hydrogen flow. Figure 5 illustrates the percent nitrous oxide destruction as a function of the hydrogen flow.
20 Figure 6 demonstrates the oxygen destruction selectivity as a function of the hydrogen flow.

EXAMPLE III

The same experiment is conducted at 25°C with a contact time of 0.7 sec with the same gas stream composition and velocity but hydrogen is partially replaced by CO (i.e., up to 50 vol.% CO). Results in terms of oxygen destruction and selectivities are the same as those
25 provided by pure hydrogen.

EXAMPLE IV

A process for purification of a nitrous oxide gas of the present invention is performed as follows:

30 A commercial SCR catalyst, Grade S-096 supplied by CRI Catalyst Company, Inc., is exposed to an adipic offgas stream of 15 slpm containing .3% NO_x, 8.0% O₂, 26.5% N₂O, .1% CO, .2% organic impurities (on a Carbon basis), and the balance inerts at an inlet temperature of

- 7 -

247°C in an isothermal pipe reactor heated by a sandbath. Space velocity is 15,000 reciprocal hours. The ammonia is fed stoichiometrically to the NO_x levels which are measured with an online NO_x analyzer. The outlet composition is as follows: .044% NO_x, 7.3% O₂, 26.5% N₂O, .2% CO, .008% organic impurities (on a Carbon basis), and the balance inerts.

CLAIMS:

1. A method for purification of a nitrous oxide gas comprising;
feeding said nitrous oxide gas and reducing agent into a de-oxidation reactor;
performing de-oxidation by reacting said reducing agent with oxygen using a de-
5 oxidation catalyst to form an inert, in order to deplete said oxygen in said nitrous oxide gas,
while limiting the amount of nitrous oxide removed from said nitrous oxide gas.
2. A method according to Claim 1, wherein said reducing agent comprises a hydrogen
containing gas, a carbon monoxide containing gas or an ammonia containing gas.
3. A method according to Claim 1, wherein said reducing agent is a hydrogen containing
10 gas.
4. A method according to Claim 1, wherein said inert comprises water, carbon dioxide or
nitrogen.
5. A method according to Claim 1, wherein said inert is water.
6. A method according to Claim 1, wherein said nitrous oxide gas comprises NO_x, nitrogen,
15 carbon monoxide, carbon dioxide or organic compounds.
7. A method according to Claim 6, wherein said NO_x is removed from said nitrous oxide
gas by selective catalytic reduction using ammonia or a precursor thereof and a selective
catalytic reduction catalyst.
8. A method according to Claim 6, wherein said carbon monoxide and organic compounds
20 are removed from said nitrous oxide gas during said de-oxidation.
9. A method according to Claim 1, wherein said nitrous oxide gas comprises adipic acid off-
gas.
10. A method according to Claim 9, wherein said off-gas comprises between 1000 ppmv and
10 vol. % oxygen, and between 100 ppmv and 1% NO_x.
- 25 11. A method according to Claim 1, wherein up to 99 vol. % of oxygen is removed from said
nitrous oxide gas.
12. A method according to Claim 1, wherein said de-oxidation catalyst comprises palladium,
platinum, or mixtures thereof.
13. A method according to Claim 7, wherein said selective catalytic reduction catalyst
30 comprises oxides of vanadium, titanium, or mixtures thereof.

- 9 -

14. A method according to Claim 1, wherein said de-oxidation step is performed with more than one reactor.

15. A method according to Claim 7, wherein said selective catalytic reduction is performed in a selective catalytic reduction reactor separate from said de-oxidation reactor.

5 16. A method according to Claim 15, wherein said selective catalytic reduction reactor is a lateral flow reactor.

17. A method according to Claim 7, wherein steam is used as a carrier gas for said nitrous oxide gas during said selective catalytic reduction.

10 18. A method according to Claim 7, wherein prior to and subsequent to said selective catalytic reduction, an oxygen containing gas is passed over said selective catalytic reduction catalyst.

19. A method for purification of a nitrous oxide gas comprising;
feeding said nitrous oxide gas and ammonia or a precursor thereof into a reactor system;
performing selective catalytic reduction by reacting said ammonia or precursor thereof
15 with NO_x in said nitrous oxide gas using a selective catalytic reduction catalyst;
feeding a reducing agent into said reactor system;
performing de-oxidation by reacting said reducing agent with oxygen in said nitrous oxide gas using a de-oxidation catalyst.

20 20. A method according to Claim 19, wherein nitrous oxide gas comprises NO_x, nitrogen, carbon monoxide, carbon dioxide or organic compounds.

21. A method according to Claim 19, wherein said reactor system comprises more than one reactor.

22. A method according to Claim 19, wherein said de-oxidation catalyst comprises palladium, platinum or mixtures thereof.

25 23. A method according to Claim 19, wherein said selective catalytic reduction catalyst comprises oxides of vanadium, titanium, or mixture thereof.

24. A method according to Claim 19, wherein said selective catalytic reduction reactor is a lateral flow reactor.

30 25. A method according to Claim 19, wherein steam is used as a carrier gas for said nitrous oxide gas during said selective catalytic reduction.

- 10 -

26. A method according to Claim 19, wherein prior to and subsequent to said selective catalytic reduction, an oxygen containing gas is passed over said selective catalytic reduction catalyst.

27. A method according to Claim 19, wherein recovery of nitrous oxide from said nitrous
5 oxide gas utilizing said reactor system comprises greater than 95%.

28. A method for purification of a nitrous oxide gas comprising;
feeding said nitrous oxide gas and ammonia or a precursor thereof into a reactor system;
performing selective catalytic reduction by reacting said ammonia or precursor thereof
with NO_x in said nitrous oxide gas using a selective catalytic reduction catalyst; while limiting
10 the amount of nitrous oxide removed from said nitrous oxide gas.

29. A method according to Claim 28, wherein nitrous oxide gas comprises NO_x, nitrogen, carbon monoxide, carbon dioxide or organic compounds.

30. A method according to Claim 28, wherein said organic compounds are selectively removed from said nitrous oxide gas stream by said selective catalytic reduction.

1/3

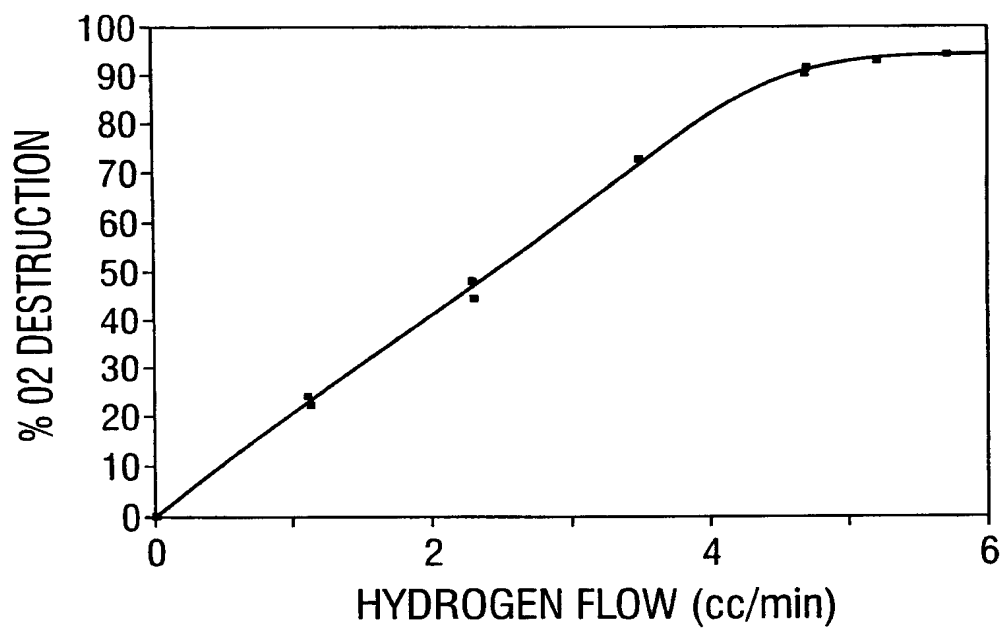


FIG. 1

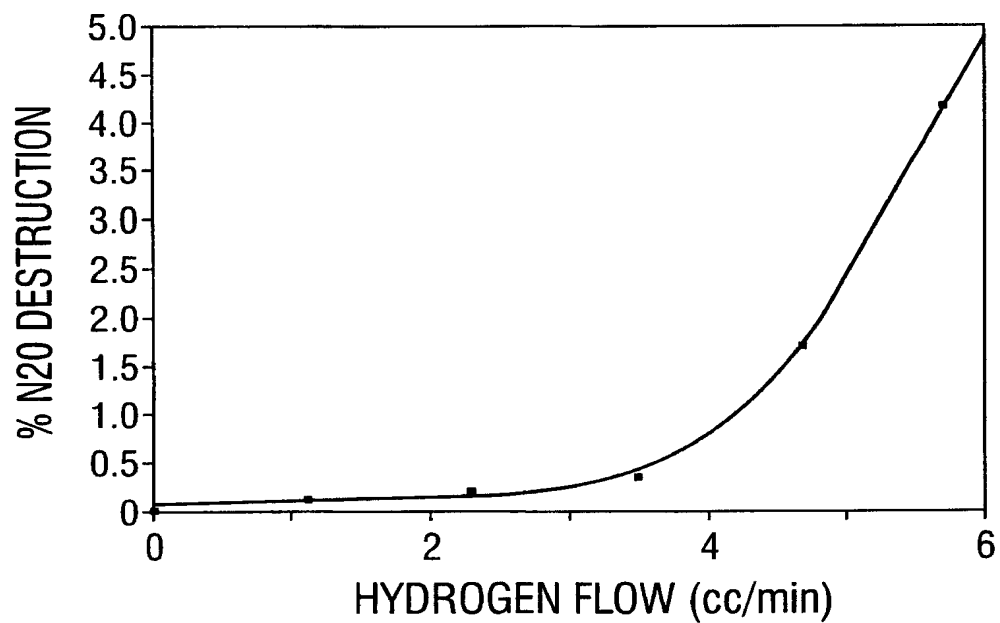


FIG. 2

2/3

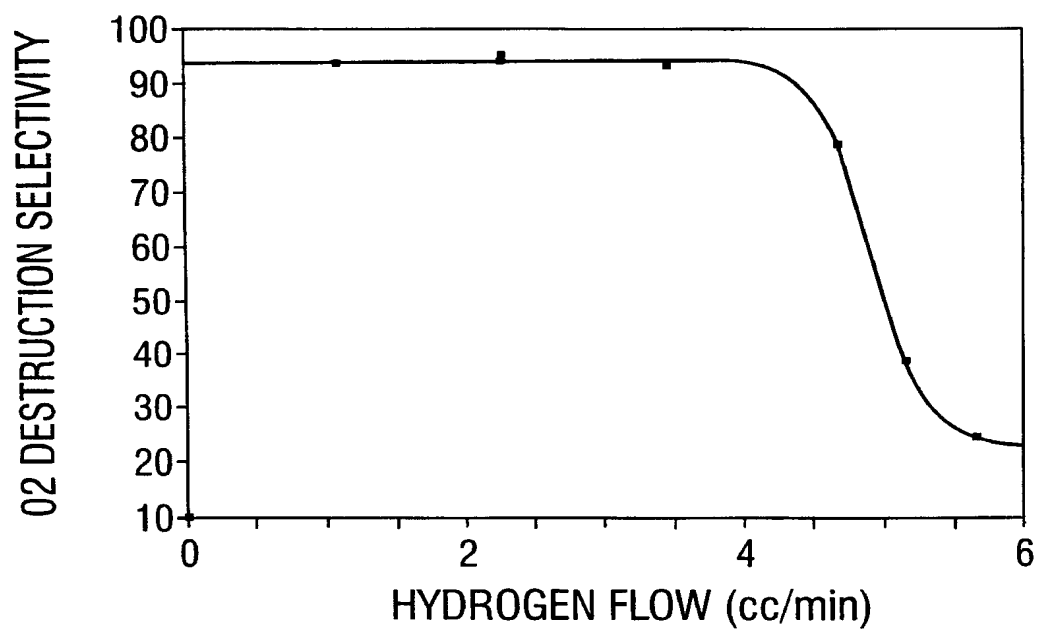


FIG. 3

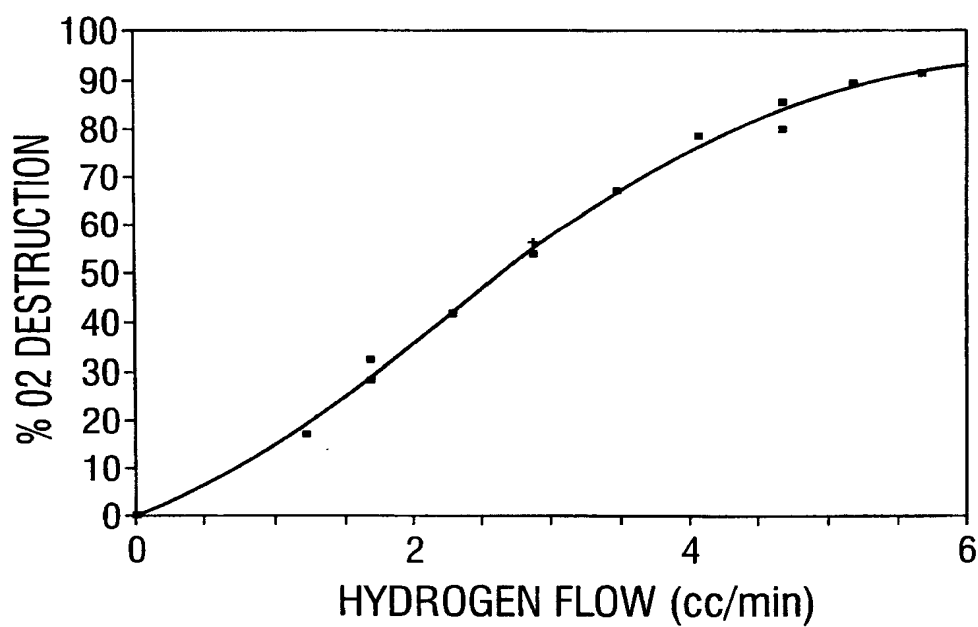


FIG. 4

3/3

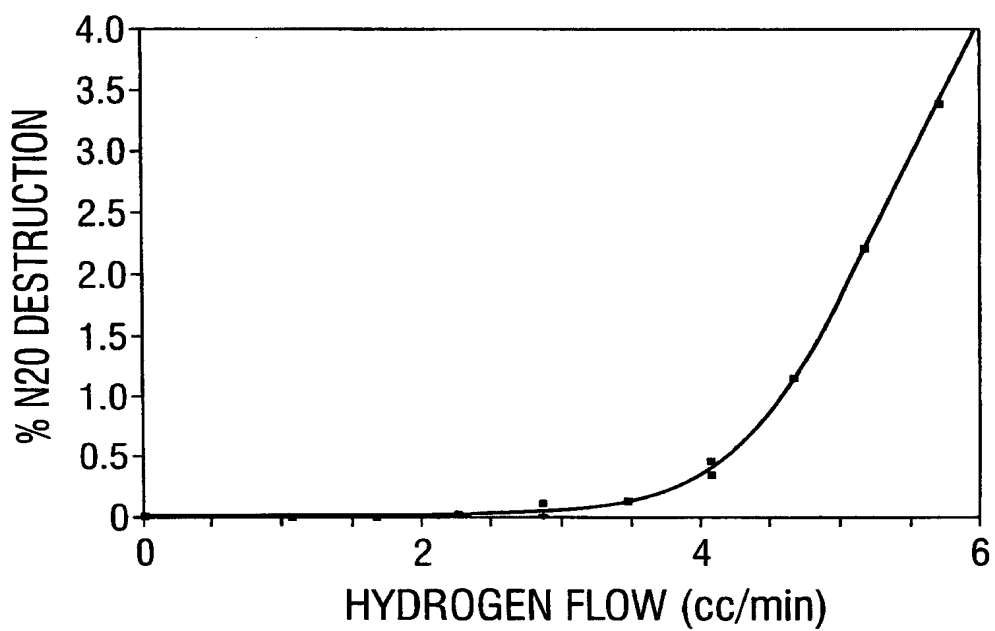


FIG. 5

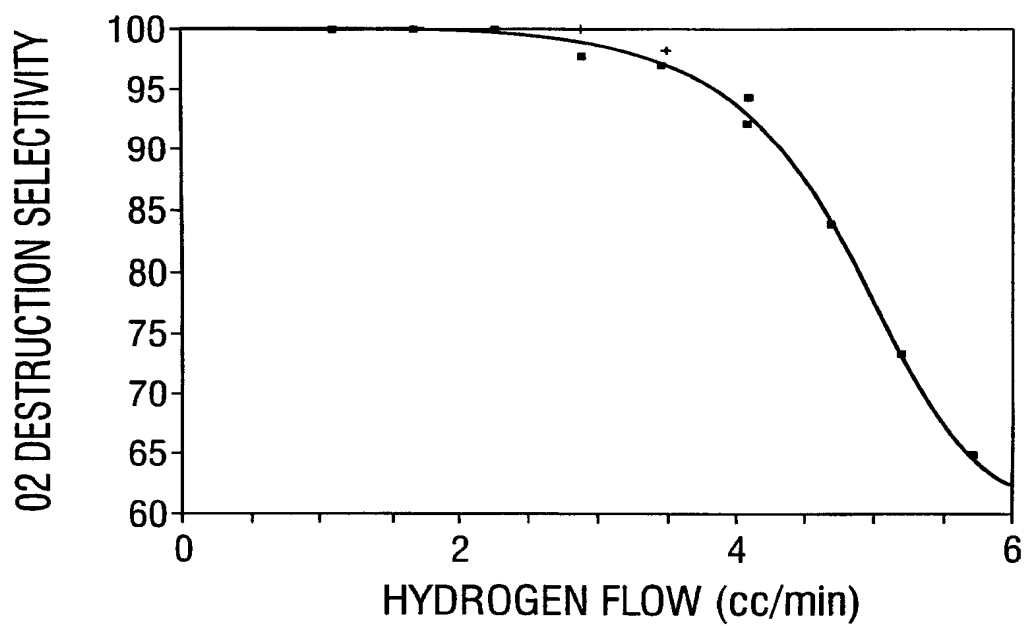


FIG. 6

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/25597

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B21/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 20 37 975 A (ZAKLLADY AZOTOWE IM. P. PRZEDSIEEBIORSTWO PANSTWOWE) 3 February 1972 (1972-02-03) page 3, paragraph 1 page 4, paragraph 1 - paragraph 2	1,5,12
Y	---	9,19-24, 27
X	EP 0 152 907 A (UHDE GMBH) 28 August 1985 (1985-08-28) claims 1-6	1,2,4-6, 8,12
X	EP 0 564 144 A (UOP INC) 6 October 1993 (1993-10-06) column 1, line 15 - line 18 column 9, line 23 -column 10, line 7	28-30
Y	---	9
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

2+ February 2000

Date of mailing of the international search report

03/03/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Eijkenboom, A

INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/US 99/25597

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 571 329 A (KATO YASUYOSHI ET AL) 18 February 1986 (1986-02-18) column 6, line 6 - line 36; figures 5,6	28-30
Y	---	19-24, 27
X	GB 1 004 741 A (THE BRITISH OXYGEN CO.) 15 September 1965 (1965-09-15) page 1, line 62 - line 66 page 3, line 12 - line 15; claims 1-3	1-5, 11, 12, 14
X	EP 0 395 221 A (BOC GROUP INC) 31 October 1990 (1990-10-31) page 4, line 7 - line 22 -----	1, 2, 4, 5, 11, 12

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/25597

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
DE 2037975	A	03-02-1972	NL	7011828 A	15-02-1972
EP 0152907	A	28-08-1985	DE	3405649 A	05-09-1985
EP 0564144	A	06-10-1993	US	5200162 A	06-04-1993
			CA	2092265 A	02-10-1993
US 4571329	A	18-02-1986	NONE		
GB 1004741	A		NONE		
EP 0395221	A	31-10-1990	AU	5077890 A	04-10-1990
			JP	2284618 A	22-11-1990
			NZ	232579 A	29-01-1992
			ZA	9000813 A	27-03-1991